Electrochemical Reduction/Oxidation in the Treatment of Heavy Metal Wastewater

Xiaolong Chen [1], Guolong Huang[2], Jiade Wang [*3]

[1, 2, *3] College of Biological & Environmental Engineering, Zhejiang University of Technology Hangzhou, P. R China

[1]xiaolongchenzj@126.com; [2]hgl03029051@163.com; [*3]jdwang@zjut.edu

Abstract

The electrochemical method is a promising technology for a clean environmental and is widely applied in the control of wastewater pollution, especially in the removal of metal and oxidation of refractory organics. The heavy metal wastewater treated by the electrochemical method is reviewed in this literature. The key and challenges of the application of the electrochemical method in the control of heavy metal wastewater are pointed out.

Keywords

Electrochemical Oxidation; Heavy Metal; Cyanide; Complex Metal; Organic Pollutants; Wastewater

Introduction

During the last two decades, with the rapid development of industries and technologies, such as electroplating industries, metallurgical industries, mining operations, fertilizer industries, power generation facilities, electronic device manufacturing units, wastewater containing heavy metals and organic pollutions compounds has been discharged into the environment increasingly, especially in developing countries. Heavy metals couldn't easy be removed from the wastewater without advanced treatment solutions. Due to their high solubility in the aquatic environments, heavy metals can be absorbed and accumulate in living organisms. If the concentration of metals in human body beyond the allowable amount, serious health disorders even the cancer could be induced. Hexavalent chromium, of particular concern because it is carcinogenic and mutagenic, diffuses quickly in soil and aquatic environment, is a strong oxidizing agent, and irritates plant and animal tissues in small quantities.

Most of heavy metals belong to persistent toxic substance (PTS). Excessive zinc could cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Copper does essential work in animal metabolism, but the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death. Nickel higher than its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis. Lead not only can cause central nervous system damage, but also damage the kidney, liver and reproductive system, basic cellular processes and brain functions.

Heavy metals pollutants are mainly discharged by electroplating wastewater, metallurgical industries, metallurgical industries and mining industries. Electroplating wastewater and metallurgical wastewater are two types of typical heavy metals water. In general, the electroplating wastewater contains a high level of heavy metals, such as copper, nickel, cadmium, chromium, zinc, silver, gold, lead and tin, acid/alkali, cyanide and organic compounds. It is nonbiodegradable, highly toxic and has a probable carcinogenic impact. The metallurgical wastewater, which is similar to the electroplating wastewater, also includes arsenic and a high concentration of suspended solid. Thus what we concern mostly is heavy metals and some nonbiodegradable organic contaminations. Heavy metal ions, which is not the unique form in the solution, could be react with NH_3 or EDTA (ethylenediaminetetraacetic acid), CN^- generate metal complex, metal cyanide, respectively. Although a lot of solutions have been investigated to treat the heavy metals such as chemical precipitation, absorption solution and ion exchange solution, metal complex and metal cyanide, it also is a challenge as these compounds couldn't be precipitated directly and transformed into metal ions easily. However, electrochemical method is a perfect solution to solve this problem and mineralize the organic compounds as well.

Electrochemical technology, one of advanced oxidation processes (AOPs), is the most promising technology for treatment of organic pollutants and heavy metals, including electrodialysis, electro-coagulation, electro-flotation, anodic oxidation and electrochemical reduction. The condition of the electrochemical

processes is moderate, without other chemical reagents added and is high energy efficiency, and is easily combined with other technologies. In this paper, four aspects will be investigated briefly: a) heavy metals recover from the liquid, b) decomposition of metal complex and metal cyanide by electrolysis, c) valence transformation of heavy metal ions by electrochemical oxidation/reduction, d) organic compounds mineralization through electrochemical technology.

Heavy Metal Wastewater Treatment by Electrochemical Technology

Metals Recover from the Liquid by Electrochemical

Recovery of heavy metals from waster is important not only in economical aspects, but also for environmental protection. Different physico-chemical treatment techniques have emerged in the last decade for the treatment of electroplating wastewater, and their advantages and limitations are also evaluated. Several electrochemical treatment techniques such as electro-coagulation, flotation, dialysis, deionization and deposition, have been investigated to remove the metals from wastewater.

D. Panias and coworkers recovered copper and nickel precipitation from acidic polymetallic aqueous solutions by the electrorecovery and neutralization. Acidic polymetallic wastewaters are generated during the pyrometallurgical treatment of chalcopyrite for the production of primary copper. Most of wastewater streams originate from the copper refining and the electrolyte regeneration stages, as well as the sulphuric acid and the precious metals plants. The feasibility of this electrorecovery was proved theoretically with the thermodynamic analysis and experimentally under various conditions. The Ni, Pb, Zn, Fe metals remain, as expected, in the solution from which nickel can be recovered with neutralization.

Le et al developed an efficient and low cost preparation method (Diazonium-Induced Anchoring Process) to graft polyacrylic acid (PAA) on the gold substrate and obtain a new PAA polymer film. As a broad-range chelating material, PAA was able to capture several heavy metal ions at low concentration. The release of those metal ions from the grafted PAA film was obtained under electro-induced-acidification by applying an anodic potential at the electrode. The electrodes coated PAA film can be used as a secondary step-treatment after conventional ion exchange process or precipitation to remove heavy metal ions from wastewater. Her later works presented the use of obtained PAA on the surface of carbon felt to remove metal ions at low concentration from wastewater, which can take place of the classical way of precipitation. Their work provided a novel strategy to meet the new criterion of "zero waste rejection" for sustainable development of environmental issues.

Decomposition of Metal Complex and Metal Cyanide by Electrolysis

The metals and complexing agents such as EDTA, NH_3, CN^- and tartarate were encountered in manufacturing printed circuit boards for electroless copper plating, metal finishing and washing effluents for remediation of metal contaminated soils. Although a lot of methods have been developed to treat the metals from wastewater, chemical precipitation is the most wildly and economically used for the treatment of metals effluents. However, the presence of strong complexing agents may make the precipitation process ineffective at even high metal levels. In addition, the high buffer capacity of complex agents requires excessive amounts of reagents to neutralize alkalinity. The electrolysis process is a meaningful, economic and feasible solution to this problem. Electrodes not only support a heterogeneous catalysis reaction place, but also aid to transporting the electronic during the process. Power supports the voltage to control the condition of process and the rate of reaction.

Juang et al used the apparatus (Fig. 1) to recover metals Cu(II) and strong chelating agents EDTA (H4L) from their molar ration of 1:1 complexed solutions. The iridium oxide coated on titanium (IrO_2/Ti) was used as the anode which obtained an economically feasible proposal that current efficiency and recovery of Cu are 60% and 95% after electrolysis only for 50 min, respectively.

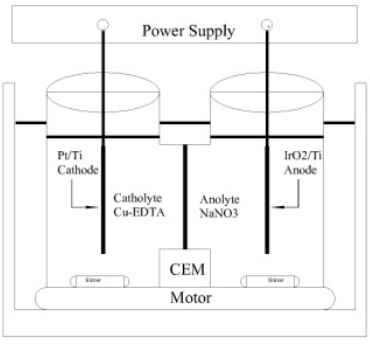

FIG. 1 SCHEMATIC OF THE ELECTROLYSIS CELL

When a current is applied to the electrolysis cell, the following oxidation reactions likely occur at the anode:

$$2H_2O \rightarrow O_2 \uparrow +4H^+ +4e \quad E^\theta = -1.229V \qquad (1)$$

$$4OH^- \rightarrow O_2 \uparrow +2H_2O+4e \quad E^\theta=-0.401V \quad (2)$$

$$2OH^- \rightarrow H_2O_2 \uparrow +2e \quad E^\theta=-0.547V \quad (3)$$

$$H_2O_2 \rightarrow O_2 \uparrow +2H^+ +2e \quad E^\theta=-0.682V \quad (4)$$

At the same time, the possible reduction reactions at the cathode are:

$$CuL_2^- +2e \rightarrow Cu(s)+L_4^- \quad (5)$$

$$O_2+2H_2O+4e \rightarrow 4OH^- \quad E^\theta=0.401V \quad (6)$$

$$2H^+ +2e \rightarrow H_2O \quad E^\theta=0V \quad (7)$$

$$2H_2O+2e \rightarrow 2H_2+2OH^- \quad E^\theta=0.828V \quad (8)$$

Where is: E^θ----standard reduction or oxidation potential.

It is obvious that the current efficiency is reduced by the main side reactions of the evolution of H_2 and O_2.

Motheo et al reported research on the removal of Cu(Ⅱ) complexed by humic acid at the concentration of 10 mg/L and 100 mg/L, respectively. A filter-press cell with $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode and stainless steel cathode was used and the differences of the performance with or without separating membrane were compared. The experimental result indicated that the main path of the removal was the electrostatic interaction with the anode followed by diffusion through the membrane and deposition at the cathode. Additionally, the degradation of humic acid contributes to the rate of Cu (II) removal. Coupled with oxidation and reduction, Cu (II) removal rate of 100 percent was achieved at current efficiencies of 75%, which showed an indication of the application to the real treatment system.

Mental wastewater containing cyanide is produced mainly due to cyanide reagent applied in gold mining, electroplating and metal finishing industries. The conventional chemical method is to oxidize the cyanide to the less harmful cyanate by using NaClO, Na_2SO_3 and H_2O_2 as oxidizing agent. Recently, the most promising strategy has been presented that CN^- could be changed into nontoxic cyanate (CNO^-) at the carbon electrode. According to the following formula, CN^- was directly (eq 9) and indirectly (eq 10) destroyed by the electrochemistry process.

$$CN^- +2OH^- \rightarrow CNO^- +2e+2H_2O \quad (9)$$

$$CN^- +HO_2^- \rightarrow CNO^- +OH^- \quad (10)$$

$$O_2+H_2O+2e \rightarrow HO_2^- +OH^- \quad (11)$$

Keith et al presented a solution that indirect electrocatalytic degradation of CN^- by exploiting the reactive oxygen intermediated formed at N-doped carbon nanotube electrodes. The removal mechanism that CN^- was reduced by HO_2^- (eq 11) was supported by cyclic voltammetry and bulk electrolysis and formation of CNO^- was confirmed via the spectroscopic method. (eq 11). The removal efficiency of the electrolysis process depended on a variety of factors such as the hydrodynamic and mass transport characteristics, features of electrodes, and power supply.

Y Gao and their coworkers used pulse current and cylinder electrodes to remove cyanide and recover high purity silver from the wastewater at the same time. Under appropriate conditions, 95.0% of cyanide removal and 99.8% of silver recover had been achieved simultaneously within 3 h, with the remaining silver less than 0.5 mg/L and cyanide less than 10.0 mg/L.

Mineralization of Organic Compounds by Electrochemical Technology

The organic compounds could be degraded directly on the electrode and indirectly with electro-generated reactive radicals such as $\cdot O_2$, H_2O_2, $\cdot OH$, Cl_2, HClO, ClO^-. The most wildly accepted mechanism on pollutant mineralization was the combustion that occurred at the surface of electrodes where $\cdot OH$ radicals are accumulated.

Electrochemical degradation of bisphenol A (BPA) on four types of anodes, Ti/BDD, $Ti/Sb\text{-}SnO_2$, Ti/RuO_2 and Pt was carried out by Yu-hong Cui et al. BPA was readily destructed at the $Ti/Sb\text{-}SnO_2$, Ti/BDD, Pt anodes, and ineffectively oxidized at the Ti/RuO_2 anode. In comparison, with its high durability and good reactivity for organic oxidation, the Ti/BDD anode appeared to be the more promising one for the effective treatment of BPA and similar endocrine disrupting chemical (EDC) pollutants.

The degradation of aspirin performed by a novel modified PbO_2 electrode assisted by H_2O_2, indicated that H_2O_2 was effective to accelerate the organic pollutants degradation. The removal of aspirin, COD and TOC reached 94%, 81%, 61% within 150 minutes treatment, respectively.

Conclusions

Compared with other methods, the advantages of the electrochemical methods included lower operating costs and less usage of extra chemical reagents and simultaneous achievements of fairly pure metals and removal of organic pollutants. Perhaps, the biggest advantage is that the electrochemical method could be easily controlled to treat the metal wastewater, and organic compounds are removed at the same time. However, more economical and activity electrodes for the treatment of special pollutions, advanced process

condition and more effectively current should be investigated.

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